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Synthesis of multi-layer graphene films on silica using physical vapour deposition

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Abstract

Carbon films and underlying copper template-layers have been deposited energetically in the same filtered cathodic vacuum arc system at 750 °C. The high quality <111> copper template-layers were supported on either silicon or silica and were subsequently sacrificially etched. On silicon, copper silicide formed during the copper deposition process, inhibiting ordered growth in the carbon film. On silica, large areas of multi-layer graphene (up to ~10 layers) oriented parallel to the substrate were synthesised and these remained intact after the sacrificial etching process. The ability to produce both copper and multilayer graphene layers in one system enables simplified fabrication of this material.

1. Introduction

The synthesis of graphene device layers on CMOS compatible substrates is advantageous for an increasing number of applications, including dye-sensitized solar cells [1], super capacitors [2], biosensors [3], nano-electronics [4] and batteries [5]. Large areas of graphene (up to 1 cm^2) have been grown on metallic templating surfaces such as copper [6]. Whilst it has been demonstrated that large area graphene can be grown on SiO_2 directly without the need for a catalyst [7] and in atmospheric pressure CVD systems [8], the growth rates achieved are so low that the growth processes take many hours to complete. A motivation for this work was to deposit graphene at moderate temperatures in short periods (minutes or less) using a scalable method. With regard to the latter, FCVA is a proven method for large scale deposition of high quality carbonaceous films [9]. Furthermore, this method would enable transfer to a wide range of substrates, requires no toxic gases and is achieved with low system cost.

Several authors have reported methods for the transfer of graphene from metallic template layers to other substrates such as silica [10,11]. An alternative approach is to grow graphene on copper films deposited onto silicon or silica [12,13]. Subsequent sacrificial etching of the copper film then enables transfer of the graphene directly onto the underlying substrate. This method of transfer reduces the probability of damage to the graphene when compared with transfer from a separate metallic foil substrate [12]. Transfer of chemical vapour deposition

(CVD) grown graphene to an underlying substrate has been demonstrated using evaporated and/or sputtered copper under-layers [12,13]. However, further simplification of the process would be achieved if the graphene and copper films could be deposited in a single vacuum system.

Previously, we reported the growth of graphene films on copper and nickel foils using the carbon plasma generated by a filtered cathodic vacuum arc (FCVA) [14]. Our results showed that the energetic carbon flux enabled graphene to grow at higher rates and lower temperatures (~750 °C) than typical for CVD. The FCVA technique can also produce other high quality films, including a range of metals, nitrides and oxides [15,16]. In particular, it is possible to prepare low roughness copper films with the preferred crystallographic orientation suitable for graphene growth [17]. Here, FCVA is used to prepare both copper under-layers and carbon over-layers with varying microstructures including that of graphene.

2. Experimental detail

The schematic in Fig. 1 shows the steps involved in synthesis of the carbon films. Silicon <100> and silica (thermal oxide 1000 nm thickness on Si) substrates were placed in the FCVA system (see Ref. [14] for details) and copper under-layers ~200 nm thick were deposited with a range of substrate biases at room temperature using a 99.99% pure copper cathode. Carbon films were then deposited on the copper under-layers at floating substrate potential (20 V) and at a temperature of 750 °C. The carbon flux was generated from a 99.99% purity 68 mm diameter carbon cathode. Relocation to the underlying silica substrate was achieved by etching the copper with ammonium persulfate ($(NH_4)_2S_2O_8$), 0.1 M).

The copper and carbon films were examined using atomic force microscopy (D3100 AFM), x-ray diffraction (XRD) and scanning electron microscopy (Nova NanoSEM). Raman spectroscopy was performed on the carbon films using a Renishaw Raman system 100 with a 514 nm Ar^+ laser and 50 μm diameter spot. Cross-sectioned samples were obtained from samples prepared using a FEI Scios focused ion beam (FIB) system and imaged using a JEOL 2100F transmission electron microscope (TEM) operating at 200 kV. The sheet resistance of the transferred graphene was measured using a four point probe.

Room temperature X-ray absorption spectra (XAS) were collected from the carbon films after transfer at the soft X-ray beamline of the Australian Synchrotron. A horizontally polarized X-ray beam was incident at angles of 20°, 55° and 90° from the surface. The signal used for the spectra was the total electron yield. The X-ray absorption near edge structure (XANES) on the carbon K-edge from graphene and graphenic carbon films includes peaks caused by 1s - π* and 1s - σ* transitions. All spectra were normalized to the intensity of the 1s - π* peak. The angular dependence of these peaks is a measure of the structural order within the material [18].

3. Results and discussion

3.1. Deposition of copper

The relationship between the substrate bias (determining the average incident ion energy [19]) and the roughness of the deposited copper films was investigated using AFM. Fig. 2

compares the surface morphology of copper films grown on silicon and silica with an earthed substrate holder (Fig. 2a and 2c) with films grown with a substrate bias of -50 V. The copper films deposited on silicon at 0 V (earthed) have an RMS roughness of 99 nm. An earthed substrate holder attracts electrons from the plasma leading to increasing temperature during deposition. The increase in deposition temperature resulted in the formation of larger agglomerates, as observed in Fig. 2a. The copper film deposited on silicon with a bias of -25 V applied had a lower roughness. As bias was applied to the substrate holder, electrons were repelled and ions were accelerated towards the growing film. The increase in the kinetic energy of the incoming ions promoted densification and reduced agglomeration, leading to smoother films. As the bias was increased to -50 V, a further reduction in the roughness was observed (Fig. 2c).

Fig. 3 shows the relationship between substrate bias and RMS roughness, measured by AFM. The roughness of films deposited onto silica wafers followed a similar trend to that observed in the films deposited on silicon. The film deposited with an earthed substrate holder was again the roughest and contained the largest copper agglomerates (Fig. 2a). As the substrate bias was increased, a reduction in the roughness of the deposited copper films was observed. In general, films deposited on silica were smoother than those deposited on silicon. Before depositing graphene, the copper films were annealed in vacuum at 750 °C as this temperature was found to be required for the growth of graphene by FCVA [14]. The insets in Fig. 2 show the morphologies of the copper films after annealing at 750 °C with enlarged agglomerates caused by Ostwald ripening during annealing.

The microstructure of the FCVA deposited copper films was measured before and after annealing using XRD and was compared against commercial copper foil (Fig. 4). Before annealing, the intensity of the (200) peak produced by the copper foil was much greater than that of the (111) peak (Fig. 4a). After annealing at 750 °C, the (111) peak produced by the copper foil was more intense (Fig. 4c), consistent with atomic reordering and increased crystallisation. It has been shown that a (111) preferred orientation leads to improved growth of graphene using CVD [20].

The copper films deposited onto silicon and silica wafers all produced a more intense (111) peak relative to the (200) peak prior to annealing (Fig. 4a and 4b). This is consistent with previously deposited FCVA copper films which showed this preferred orientation [17].

After annealing, the copper films deposited on silicon retained the more intense (111) peak (Fig. 4c). However, peaks attributed to copper silicide (Cu_3Si) were observed, showing that the copper reacted with the underlying silicon during annealing. By contrast, the intensities of the (111) and (200) peaks in the diffractograms from the copper films grown on silica did not change markedly following annealing and no Cu_3Si peaks were produced (Fig. 4d). Hence, we assert that the copper layer did not react with silica due to the thermal stability of the latter [21].

A cross-sectional TEM image of the copper film deposited onto silicon with 50 V bias applied is shown in Fig. 5a. This confirms the presence of copper silicide and supports the AFM measurements showing higher roughness in the copper films on silicon post annealing. The

corresponding TEM image of the copper film deposited onto silica with a -50 V bias (Fig. 5b) confirms the lack of copper silicide formation. Unlike the copper film on silicon, the copper film on silica appears continuous and homogenous.

3.2. Deposition of carbon

The microstructure of the carbon deposited using FCVA onto the annealed copper/silicon and copper/silica substrates was examined with Raman spectroscopy, shown in Fig. 6. Peaks in the Raman spectra located at ~1350 cm^{-1} and ~1580 cm^{-1} are often observed in nano and micro crystalline graphitic materials and are referred to as the D and G peaks. These peaks can be attributed to the defective edges and defect-free centre of graphene layers respectively [22]. The formation of graphene is indicated when the D and G peaks are observed in conjunction with the 2D peak located at ~2700 cm^{-1}. Both the intensity (2D/G) and defect (D/G) ratio, are common methods for indicating the number of layers and quality [22]. All spectra from carbon films deposited on copper/silicon feature a prominent 'D' peak, indicating a significant defect density (Fig. 6a). A well resolved 'G' peak was visible in all spectra. None of the carbon films exhibited intense 2D peaks, indicating that ordered graphene was not produced on copper/silicon. The lack of graphene growth is likely caused by the presence of copper silicide and/or high surface roughness (Figs. 2 and 3). Rather, the spectra resemble those from disordered microcrystalline graphitic material [23].

The Raman spectra from the carbon films deposited at 750 °C onto copper/silica feature well resolved, D, G and 2D peaks (Fig. 6b). The carbon film deposited on the copper film grown "earthed" has the largest D:G peak, defect ratio (I_D/I_G) and the smallest intensity ratio (I_{2D}/I_G), most likely a consequence of the increased roughness of the copper. A decrease in the defect ratio and an increase in the intensity ratio is observed in the spectra from the film grown on copper deposited with -25 V bias. The defect ratio decreases and the intensity ratio increases further in the spectra from the carbon films deposited with -50 V and -75 V bias. The presence of the intense 2D peak in all spectra are indicative of ordered graphene. The I_{2D}/I_G for the carbon film deposited on copper/silica biased at -50 V was 1.2 which corresponds to approximately 10 layers or more of graphene.

3.3. Transfer of graphene

It is clear from Fig. 6 that graphene was only grown on the copper/silica substrates. The graphene grown on the copper deposited onto silica using -50 V substrate bias was transferred to the underlying silica by sacrificially etching the copper under-layer. Fig. 7 shows (a) the optical and (b) SEM images of the transferred multilayer graphene. The carbon film is continuous over a large area (~1mm^2). A sheet resistance value of 14.1 kΩ/□ was measured from the transferred graphene film using the four point probe. This value is similar to values report previously for FCVA deposited graphene grown on and transferred from copper foil [14].

Raman spectra were used to assess the quality of the multilayer graphene before and after transfer to the underlying silica substrate (Fig. 8). After the transfer, an increase in the D peak and a reduction in the 2D peak were observed. These changes indicate an increase in the

number of defects and an increase in the number of layers. This is consistent with the bending and folding visible in Fig. 7b.

Fig. 9 shows carbon K-edges from the transferred multilayer graphene supported on silica (after sacrificial etching of the copper) at varying incident angles. The XANES shows two main features: the 1s - π* peak at ~285 eV (indicated by an arrow) and the 1s - σ* peak at ~ 292 eV. The doublet in the 1s - σ* peak indicates that well-ordered graphitic layers are present [18]. In addition, there is a strong angular dependence of the ratio of intensities of the 1s - π* and 1s - σ* peaks. This is a result of the interaction of the polarised x-ray beam and the highly directional bonds in graphene-like materials [18]. Furthermore, the inset in Fig. 9 shows that there is a linear dependence of the 1s - π* peak intensity (when the spectra are normalised to the 1s - σ* peak) as a function of $\cos^2\theta$. This is as expected for ordered graphene oriented parallel to the substrate [18].

4. Conclusion

Energetic deposition has been used to produce copper template layers on silicon and silica substrates. Subsequent energetic deposition of carbon onto these template layers at 750 °C produced films with structural properties that strongly depend on the structure of the copper templates. Multilayer graphene was deposited onto copper/silica. Formation of the copper silicides prevented this material growing on copper/silicon. The ability to produce high quality copper template under-layers and multilayer graphene using a single deposition method enables simplified fabrication of this technologically important material.

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Figures

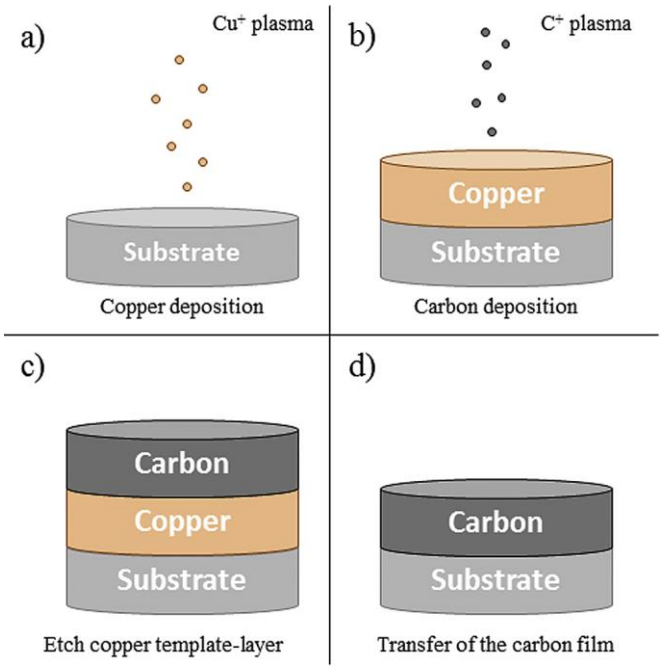

Fig. 1. Schematic showing the growth sequence and transfer process employed to fabricate carbon films on silicon/silica substrates.

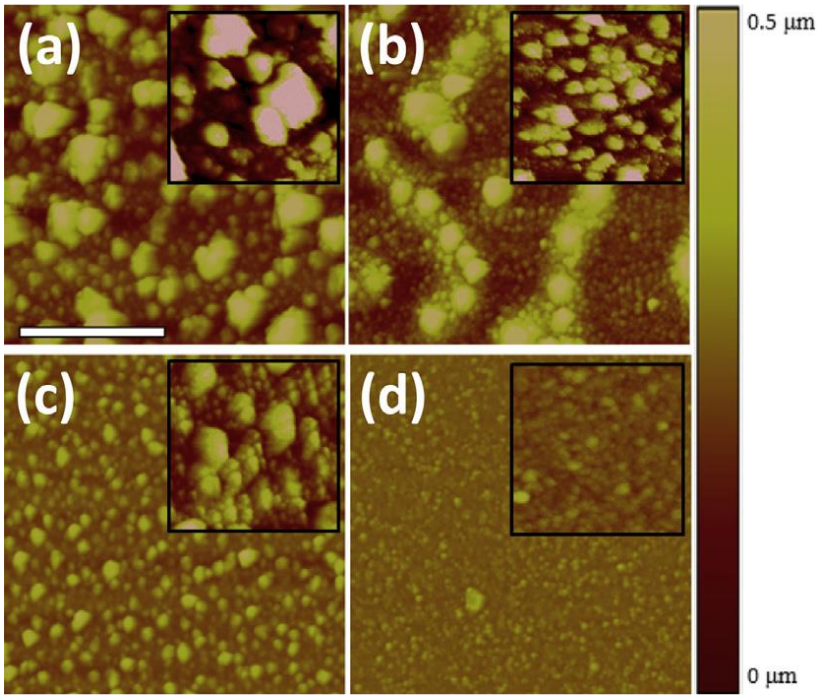

Fig. 2. Atomic force micrographs of copper template layers energetically deposited onto silicon (top row) and silica (bottom row) with the substrate holder earthed ((a) and(c)) and biased at -50 V ((b) and (d)). Insets show the morphology of the films after annealing at 750 °C for 10 min. The scale bar is 3 µm in length.

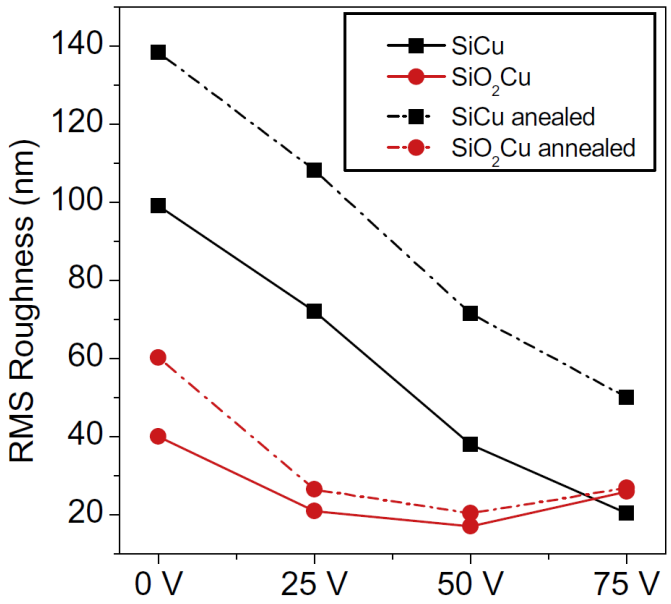

Fig. 3. RMS roughness of copper films deposited on silicon and silica by FCVA before and after annealing.

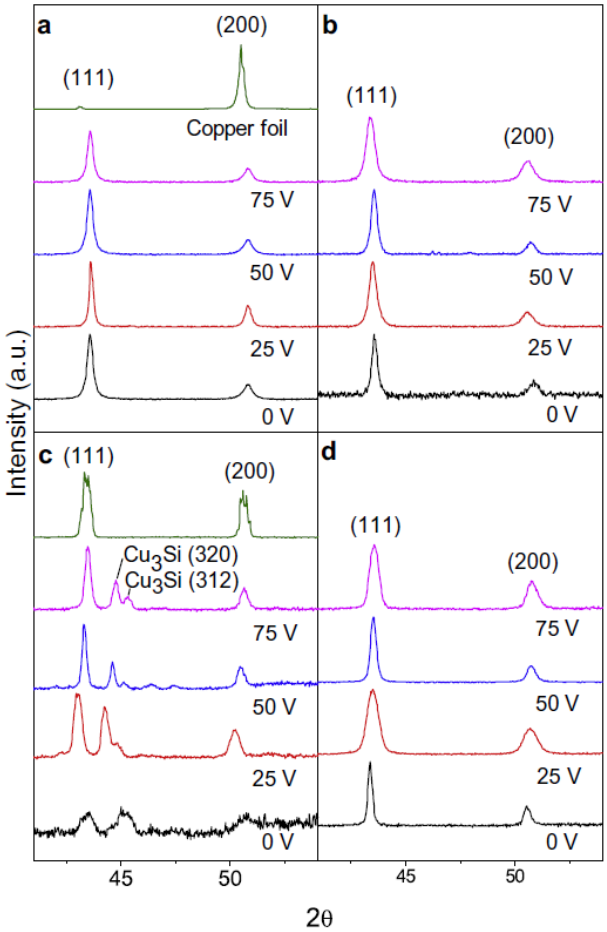

Fig. 4. X-ray diffractograms from copper films supported on (a) silicon and (b) silica at the substrate bias voltages indicated. (c) and (d) show the corresponding diffractograms after annealing at 750 °C. Also shown for comparison in (a) and (c) are diffractograms from a copper foil.

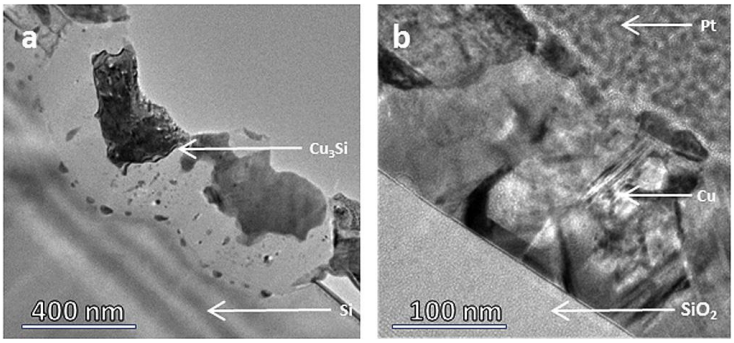

Fig. 5. Cross-sectional TEM images showing the copper grown with a -50 V substrate bias on (a) silicon and (b) silica. Various features are labelled.

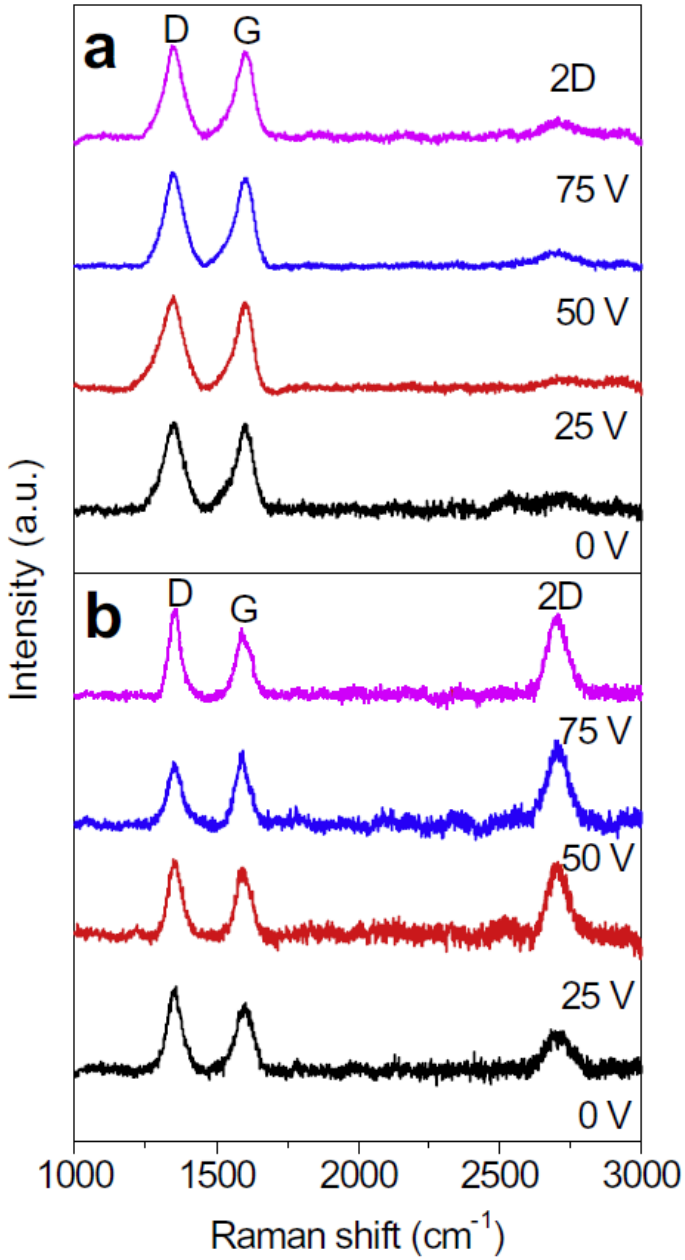

Fig. 6. Raman spectra from carbon deposited onto (a) copper/silicon and (b) copper/silica. The bias voltages shown are those used for the deposition of the copper underlayer.

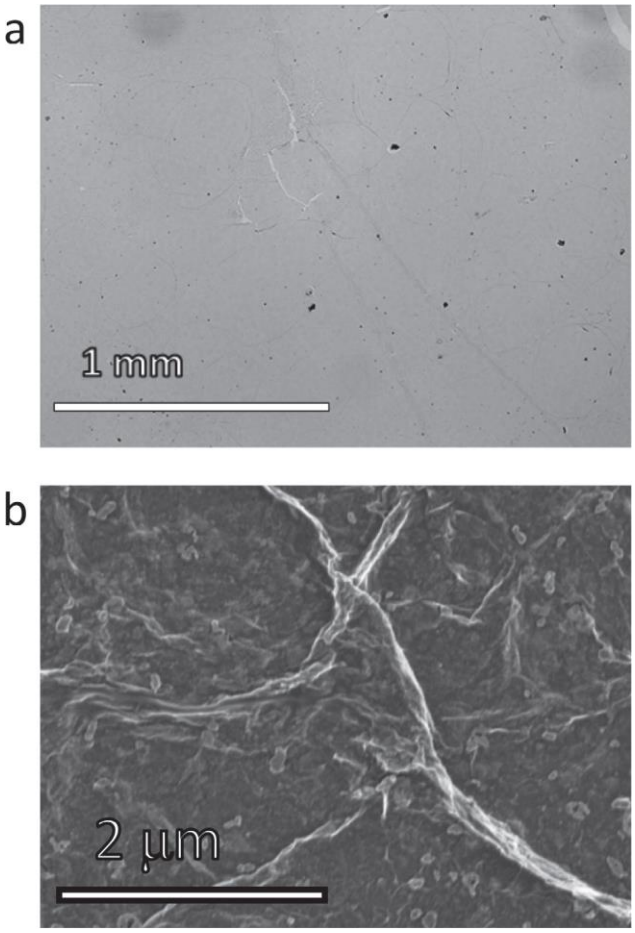

Fig. 7. (a) Optical and (b) SEM images of a FCVA deposited multilayer graphene film after sacrificial etching of the copper under-layer (deposited using -50 V substrate bias) and transfer to silica.

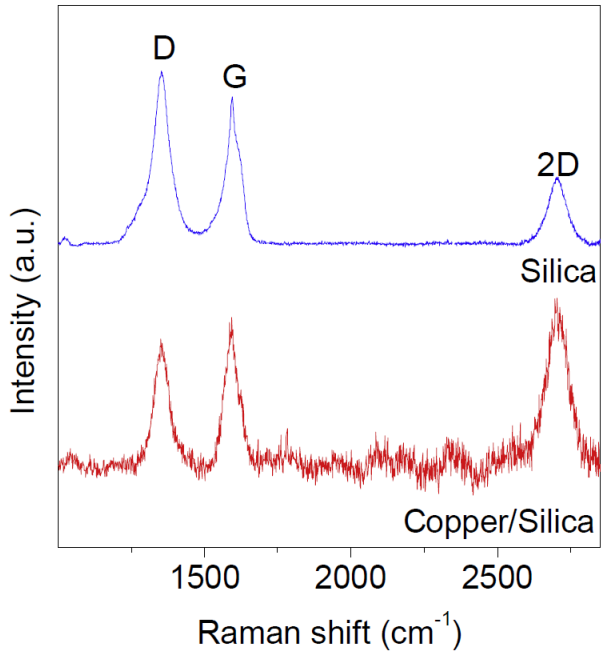

Fig. 8. Raman spectra from multilayer graphene on copper/silica (before transfer) and on silica (after transfer by sacrificial etching of copper).